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VARIATION OF THE ADIABATIC ELASTIC CONSTANTS

OF ALUMINUM WITH TEMPERATURE

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Abstract

The elastic constants of a single crystal of aluminum have been measured by the pulsed ultrasonic technique in the temperature range from 80° to 300° K. It was found that all of the elastic constants decreased linearly with increasing temperature in this range and had the following values for the slopes.

$$\frac{\Delta C_{44}}{\Delta T} = -1.43 \times 10^8 \quad \text{dyne cm}^{-2} \text{ deg}^{-1}$$

$$\frac{\Delta C'}{\Delta T} = -1.23 \times 10^8$$

$$\frac{\Delta K}{\Delta T} = -1.8 \times 10^8$$

The values of the elastic constants at room temperature (298°) were found to be: $C_{44} = 0.2848$, $C' = 0.234$ and $K^{-1} = 0.770$ all expressed in units of 10^{12} dyne cm^{-2}.

A thermodynamic argument is used to separate the effects of the volume change through thermal expansion from the other effects of temperature on the elastic constants. This argument shows that the change with temperature cannot be explained solely in terms of the change in volume because there is an explicit dependence of the constants of temperature. This explicit dependence is different in both magnitude and direction for the shear constants C' and C_{44}.

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Introduction

The dependence on temperature of the adiabatic elastic constants of a single crystal has been studied at low temperatures for several ionic crystals (e.g. K Br[1] and Na Cl[2,3,4]) and for some alloys (e.g. Beta Brass[5]). Sodium has also been studied[6] in this range of temperature verifying Fuch's[7] theory for the elastic constants of that metal.

1. J. K. Galt, Phys. Rev., 73, 1460 (1948)

2. W. C. Overton and R. T. Swim, Phys. Rev., 84, 758-762, (1951)

3. F. C. Rose, Phys. Rev., 49, 50, (1936)

4. M. A. Durand, Phys. Rev., 50, 449, (1936)

5. J. S. Rinehart, Phys. Rev., 59, 308 (1941)

6. Siegel and Quimby, Phys. Rev., 54, 293, (1938)

7. K. Fuchs, Proc. Roy. Soc., A157, 444 (1936)

A theoretical treatment of the elastic constants of aluminum has recently been published[8] making it desirable to know not only the experimental values at room temperature[9,10] but also the low temperature values as

8. R. S. Leigh, Phil. Mag., 62, 139 (1951)

9. Goens, Ann. d. Physik., 17, 233 (1933)

10. D. Lazarus, Phys. Rev., 76, 545 (1949)

well. To this end the study of aluminum in the temperature range from 80° to 300° K. has been undertaken.

The development since the war of the ultrasonic pulse technique has provided a particularly adaptable means of measuring the elastic constants as a function of temperature. This method is also capable of more accurate determinations than was possible with the earlier methods which were used in a large percentage of the work reported in the literature.

Experimental Procedure

A single crystal of aluminum was obtained from Dr. John R. Neighbours of this laboratory. This crystal was grown by him from the melt in the form of a cylinder 5/8" in diameter and approximately 1.23 cm. in length. The orientation of the axis of the cylinder is very close to [110] with direction cosines l = 0.72708, m = 0.68223, n = 0.06423 with respect to the cubic axes. The two end faces of the cyliner were polished plane and parallel to within 0.001 cm.

An ultrasonic pulse technique was used to measure the elastic constants and the electronic equipment necessary for this has been adequately described in other papers[10,11] and needs no further elaboration here.

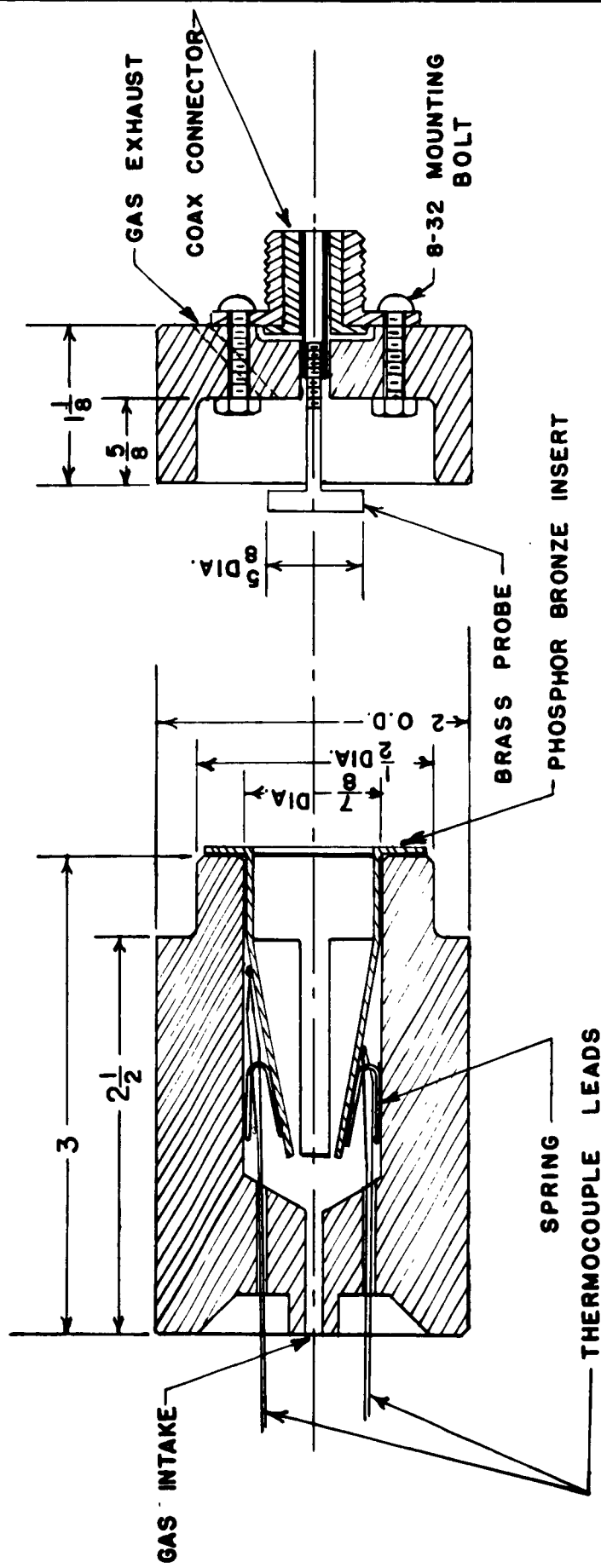11. J. W. Burns, Masters Thesis, TM 88, Case Institute of Technology (1952)

In order to provide controllable temperatures for the crystal and simultaneous measurements of the elastic constants, a lucite cryostat was designed, the essentials of which are shown in figure 1. Boiling liquid nitrogen was used as the coolant in the following manner. The nitrogen was held in a Purox liquid gas container which was connected with insulated tubing to the gas intake of the cryostat. A 100 watt heating element connected to a "Variac" was immersed in the liquid nitrogen and this provided a controllable evaporation rate for the nitrogen. With various types of shielding for the cryostat and different rates of evapo-ration, any desired temperature between room temperature and about -170° C. could be obtained and maintained. Measurements were made at liquid nitro-gen temperatures by immersing the cryostat in a dewar of liquid nitrogen. Temperature measurements were made with two Chromel p-alumel thermocouples

mounted as shown in figure 1 just above and below the position of the alumi-
num crystal within the cryostat. In none of the runs did a temperature
gradient of more than a degree appear across the specimen.

Sound waves were generated within the aluminum in the usual manner
for the ultrasonic pulse technique in which a round, 10 megacycle quartz
crystal 1/2" in diameter was attached to one face of the specimen and
excited electrically to produce the acoustic waves within the specimen.
An x-cut quartz was used to generate longitudinal waves and a y-cut quartz
was used for the two shear waves.

The choice of the adhesive with which to attach the quartz presented
a problem. At room temperature, phenyl salicylate proved to be a very
satisfactory adhesive. In the temperature range from -25° to -125° C.
many substances were tried including various grades of stopcock grease,
phenyl salicylate, light instrument oil, allyl chloride, and rubber
cement, but the most satisfactory adhesive proved to be a mixture of
rubber (10% by weight) in vaseline. For measurements from -100° to
-196° C. Dow Corning Compound 5 Black Silicone Grease gave very good
results.

The method derived for applying the quartz was to place a small
amount of the cement on the face of the aluminum and then to place the
quartz on top of this. The cement was pressed into a very thin uniform
film and the quartz appropriately oriented with respect to the specimen
crystalographic axes. This assembly was then placed on the flat brass
probe of the cryostat so that the brass made contact with the quartz.
The two sections of the cryostat were slipped together at room tempera-
ture, care being taken to assure that the relative orientation of quartz
and specimen was undisturbed. Inside the cryostat, the aluminum made
ground contact with the spring-loaded "fingers" of the phosphor bronze

GAS EXHAUST

COAX CONNECTOR

8-32 MOUNTING BOLT

$1\frac{1}{8}$

$\frac{5}{8}$

$\frac{5}{8}$ DIA.

BRASS PROBE

PHOSPHOR BRONZE INSERT

2 O.D.

$2\frac{1}{8}$ DIA.

$\frac{7}{8}$ DIA.

$2\frac{1}{2}$

3

SPRING

THERMOCOUPLE LEADS

GAS INTAKE

LUCITE CRYOSTAT

insert which in turn made contact through the 8-32 mounting bolts to the coaxial connector and then to the shield of the coaxial cable. The cryostat was finally connected to the insulated tubing and the electrical connections were made for the required measurements.

When making measurements at a particular temperature, the procedure was first to calibrate the time base of the sweep of the DuMont 256-D C. R. O. in the manner prescribed by the manufacturer. The pattern of the echoes as observed on the 100 microsecond A sweep was photographed for record and the readings from the thermocouples recorded. Readings of the time delay of the R sweep as shown on a dial of the C. R. O. were recorded for the position of the leading edge of each echo out to 100 microseconds delay. The readings were repeated five times for this temperature, the desired temperature being maintained and recorded through- out the readings. At the conclusion of this, the specimen was brought back to room temperature and the quartz removed. This general procedure was followed at least three times for each of the two shear and one longi- tudinal waves propagated within the aluminum.

A modulation pattern superimposed on the echo pattern was observed for all of the measurements. This modulation was much more pronounced for the shear waves than for the longitudinal waves and was invariant to small changes of the driving frequency. It is thought that this effect is due to non-parallelism in the specimen, but it did not destroy the accuracy of the results.

The first set of measurements were made at 173° K. in the manner outlined above, but, in addition, measurements were also made at this temperature with a dummy quartz crystal cemented to the other end of the specimen and oriented in the same manner as the driving crystal. This was done in order to determine the time required for the ultrasonic

pulse to traverse the distance of the cement and the quartz and then be reflected from the quartz instead of the aluminum face. The transit time correction (always approximately 0.10 microsecond) thus obtained is then subtracted from the transit times obtained in the original measurements to give the transit time of the accoustical waves in just the aluminum. When this data taken at $173°$ K. was analyzed, it was found that the results of the measurement of the transit time in the aluminum alone were most consistent when a constant transit time error of 0.100 microsecond was used. Burns[11] observed a much smaller transit time correction than this in his measurements on Cu Si, but in this case there was a decided difference in the impedance of the Cu Si and the quartz. Aluminum appears to have nearly the same impedance to the pulse as the quartz and in this case the transit time correction is the time required for the pulse to travel the thickness of a 10 megacycle quartz, i. e. 0.100 microsecond. For all subsequent measurements at other temperatures, a constant transit time correction of this amount was assumed.

From measurements of the length of the aluminum crystal and the time required for the ultrasonic pulse to traverse this length, the velocity of the pulse in the medium could be computed. The length of the specimen was corrected for thermal expansion by using these values of the thermal coefficient of expansion[12].

$$\alpha = 0.23 \times 10^{-4} \text{ between } 0° \text{ and } 25° \text{ C.}$$

$$\alpha = 0.22 \times 10^{-4} \text{ between } -78° \text{ and } 0° \text{ C.}$$

$$\alpha = 0.185 \times 10^{-4} \text{ between } -191° \text{ and } 16° \text{ C.}$$

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12. Landolt-Bornstein, Physikalische-Chemische Tabelle. Hw II, P. 1217

The density of the aluminum was computed from the x-ray lattice parameter data[13] which was

$$a = 4.0495 \text{ Angstroms at } 25^\circ \text{ C.}$$

and was appropriately corrected for thermal expansion.

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13. Barrett, "Structure of Metals", McGraw-Hill, New York 1943, p. 552

The elastic constants were calculated by using the perturbation method developed by J. R. Neighbours and Charles S. Smith[14], but, because

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14. J. R. Neighbours and Charles S. Smith, J. A. P. Vol 26, No 12, 1338-1339, (Dec. 1950)

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of the particular orientation of this crystal, the first approximation of the constants was good to within the limits of the accuracy of these data.

The actual formulae used in the calculation of the elastic constants are:

$$\rho V_1^2 = C_{11} - 2\left[l^2 m^2 + m^2 n^2 + n^2 l^2\right] C$$
$$\rho V_2^2 = C_{44} + 2\, l^2 m^2 \left[l^2 + m^2\right]^{-1} C \tag{1}$$
$$\rho V_3^2 = C_{44} + 2\, n^2 \left[l^4 + l^2 m^2 + m^4\right]\left[l^2 + m^2\right]^{-1} C$$
$$C = C_{11} - C_{12} - 2C_{44}$$

Where V_1 is the velocity of longitudinal waves,

   V_2 is the velocity of shear waves with particle motion
       in the $[\bar{1}10]$ direction,

   V_3 is the velocity of shear waves with particle motion
       in the $[001]$ direction.

   ρ is the density of the aluminum at the temperature
       involved in the measurements.

   l, m, n are the direction cosines of the crystallographic axes with

respect to the aluminum specimen axis.

In addition, the constants C' and K^{-1} are defined as

$$C' = 1/2 \left(C_{11} - C_{12} \right)$$
$$K^{-1} = 1/3 \left(C_{11} + 2C_{12} \right)$$

Results:

Although Koster[15] measured Young's Modulus (E) for polycrystalline rods of aluminum as a function of temperature and found that in the range of -180° to 0° C E decreased linearly with increasing temperature with a slope of -2.94 x 10^8 dynes/cm^2, no data for the elastic constants has been found. Several investigators[9,10,16] have measured the elastic constants of aluminum at room temperature, however, and their results are compared with the present results in Table 1. From this table it may be seen that the present results compare very well with those obtained earlier by Goens[9] and Garr[16], but rather unfavorably with those of Lazarus[10]. This discrepancy with Lazarus' values is significant, especially since Leigh[8] used these results as the basis for his theoretical work on aluminum.

The experimentally obtained values of ρV^2 at five different temperatures are presented in Table 2. These values were substituted in equations (1) to obtain the elastic constants C_{12}, C_{44}, and C_{11}, and then C' and K^{-1}. It is interesting to note that although the elastic constants relating to the two shear directions change with temperature, the ratio of these two quantities, the anisotropy, is constant over the temperature range investigated.

Figure 2 shows the linear variations of the two shear constants, C_{44} and C' with temperature.

Figure 3 gives the temperature dependence of the reciprocal compressibility. The departure from linearity at 173° and 146° K. are due to the

experimental error in C_{11} since

$$K^{-1} = \frac{C_{11} + 2 \, C_{12}}{3}$$

This variation is still less than half a percent.

Since it was found that the elastic constants decrease linearly with increasing temperature, the value of the constant at some temperature T may be written in the following form:

$$C_T = C_o + \frac{\Delta C}{\Delta T} \, T$$

The temperature coefficient of the elastic constants $\frac{\Delta C}{\Delta T}$ is just the slope of the line on the elastic constants versus temperature curve. These are presented in Table 3.

The results of the determinations of the elastic constants are accurate to within 0.5%. This was determined by carrying the probable error of the velocity and density measurements through the formulas used for the calculation of the elastic constants. The probable errors of the elastic constants computed in this manner were in no case greater than 0.3%. This treatment does not consider the probable error involved in the orientation of the specimen axis with respect to the principal axes of the crystal lattice. This omission was felt to be legitimate since the internal check on the sum of the squares of the direction cosines, i.e. $l^2 + m^2 + n^2 = 1$, is very good. However, admitting that this is a source of error, it still seems safe to say that accuracy of these values is within 0.5%.

Table 1 - Comparison of the values of the elastic constants of aluminum at room temperature obtained by various investigators. Results are expressed in units of 10^{12} dyne cm.$^{-2}$ except in the case of the anisotropy.

Investigator	C_{11}	C_{44}	C_{12}	K^{-1}	C'	Anisotropy $\dfrac{2\,C_{44}}{C_{11} - C_{12}}$
This paper	1.082	0.2848	0.613	0.770	0.234	1.21
Goens	1.082	0.284	0.622	0.775	0.230	1.24
Lazarus	1.056	0.285	0.639	0.778	0.209	1.37
Garr	1.073	0.282	0.605	0.760	0.234	1.21

Table 2 - Values of ρ and ρV^2 for aluminum at various temperatures

V_1 is the velocity of longitudinal waves in the $[110]$ direction.
V_2 is the velocity of shear waves with particle motion in the $[1\bar{1}0]$ direction.
V_3 is the velocity of shear waves with particle motion in the $[001]$ direction.

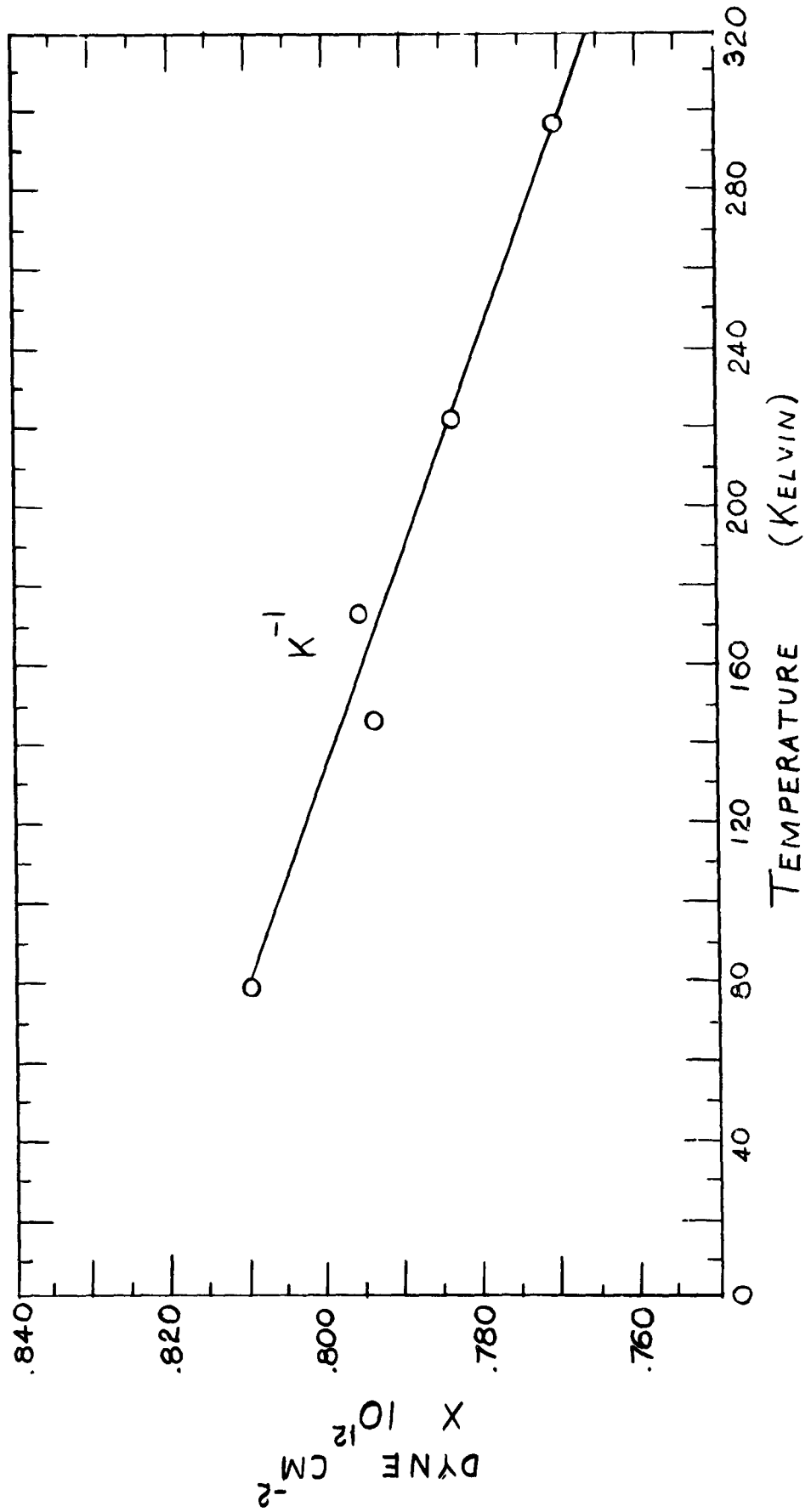| Temperature	ρ (g. cm.$^{-3}$)	ρV_1^2 (x 10^{12} g. cm.$^{-1}$ sec.$^{-2}$)	ρV_2^2	ρV_3^2
298° K.	2.698	1.133	0.2349	0.2842
223° K.	2.711	1.162	0.2454	0.2961
173° K.	2.716	1.184	0.2515	0.3030
146° K.	2.721	1.186	0.2538	0.3069
78° K.	2.743	1.214	0.2636	0.3153
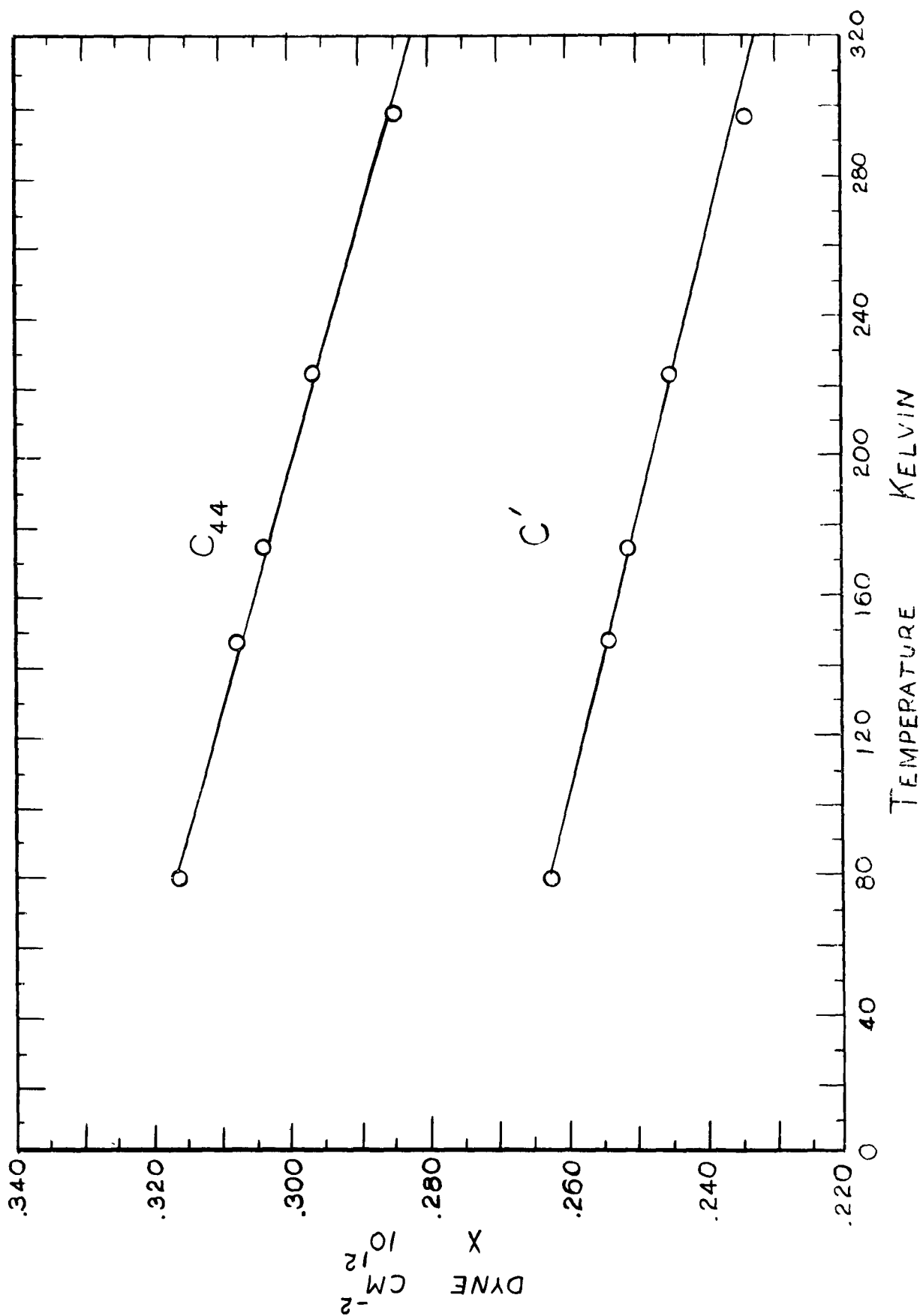
Fig. 3 Temperature Variation of the Reciprocal Adiabatic Compressibility

Table 3 - Temperature coefficients of the elastic constants in the range from 80° to 300° K., expressed in units of dyne $cm.^{-2}$ deg.$^{-1}$

$$\frac{\Delta C_{44}}{\Delta T} \approx -1.43 \times 10^{8}$$

$$\frac{\Delta C'}{\Delta T} \approx -1.33 \times 10^{8}$$

$$\frac{\Delta K^{-1}}{\Delta T} \approx -1.8 \times 10^{8}$$

Discussion

As a start on the problem of understanding the variation of the elastic constants with temperature, one can develop a thermodynamic argument to separate the effect of temperature alone from the accompanying changes in volume due to thermal expansion.

Thinking of the elastic constants as a function of two thermodynamic variables T and P, one can take the total derivative of C(T,P) and, making appropriate substitutions, arrive at

$$\frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_V = \frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_P + \frac{\beta K^{-1}}{C}\left(\frac{\partial C}{\partial P}\right)_T \qquad (2)$$

The left hand side of this equation expresses the change in the elastic constant with temperature one might expect if there were no change in volume i.e. this is the explicit dependence of the constant on temperature at constant volume. $\frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_P$ is a quantity which was measured in the work of this paper, and involves the dependence of the constant on T both directly and indirectly. $\frac{\beta K^{-1}}{C}\left(\frac{\partial C}{\partial P}\right)_T$ is thus a measure of the indirect dependence on temperature through the volume thermal expansion coefficient β. K^{-1} is the reciprocal isothermal

compressibility. The quantity $\left(\dfrac{\partial C}{\partial P}\right)_T$ has been measured by Lazarus[10].

The quantities $\left(\dfrac{\partial C}{\partial P}\right)_T$ were obtained from Lazarus' paper by working with his original velocity measurements; V_1, V_2, and V_3.

Let

$$Y_1 = \rho V_1^2$$
$$Y_2 = \rho V_2^2 \qquad\qquad (3)$$
$$Y_3 = \rho V_3^2$$

Now in Lazarus' work

$$Y_1 = C_{11}$$
$$Y_2 = 1/2 \left(C_{11} - C_{12} + 2C_{44} \right) \qquad\qquad (4)$$
$$Y_3 = C_{44}$$

In the accompanying graphs Y_1, Y_2, and Y_3 are plotted against P and a least squares slope is drawn through the resulting points. This yields

$$\frac{dY1}{dP} = Y_1' = 9.40 \times 10^{-12}$$

$$\frac{dY2}{dP} = Y_2' = 6.23 \times 10^{-12}$$

$$\frac{dY3}{dP} = Y_3' = 2.33 \times 10^{-12}$$

Now these may be used to find

$$\left(\frac{\partial C_{44}}{\partial P}\right)_T = Y_2'$$

$$\left(\frac{\partial C'}{\partial P}\right)_T = Y_1' - Y_2' + Y_3'$$

$$\left(\frac{\partial K^{-1}}{\partial P}\right) = \frac{1}{3} Y_1' + \frac{4}{3} Y_2' - \frac{4}{3} Y_3'$$
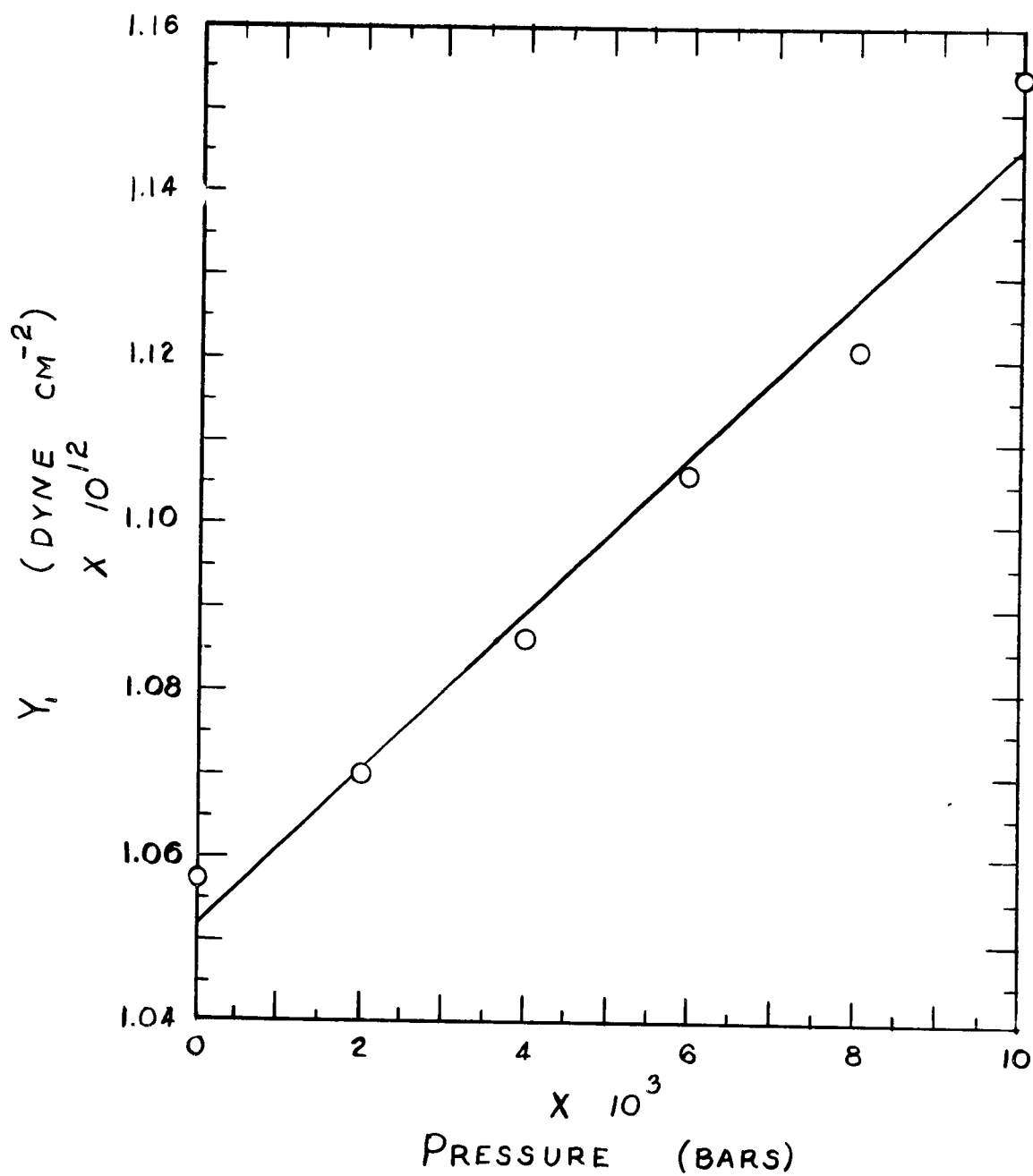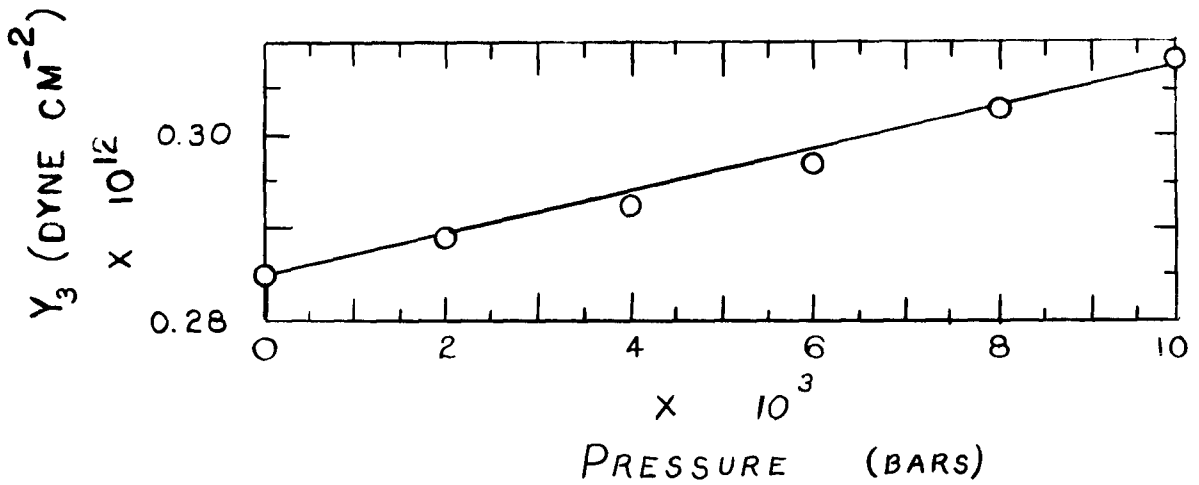
Fig. 4 Pressure Dependence of Y_1 (Lazarus)

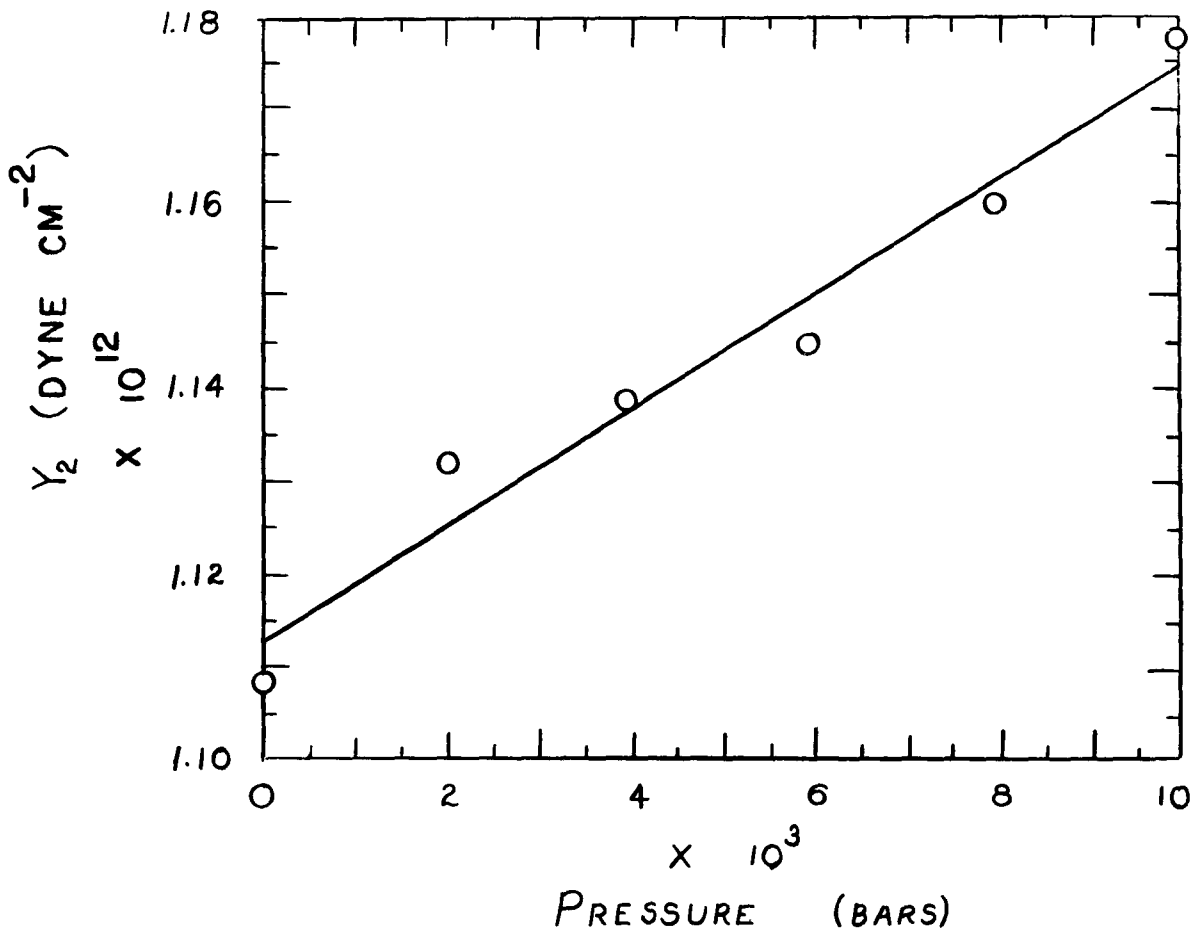Fig. 5 Pressure Dependence of Y_3 (Lazarus)

Fig. 6 Pressure Dependence of Y_2 (Lazarus)

In evaluating equation (2), the present results are taken as the correct room temperature values. The appropriate value of β is 6.9×10^{-5} deg^{-1} and the isothermal compressibility as calculated from this paper's value of the adiabatic compressibility is $K = 1.36 \times 10^{-12}$ cm^2 dyne^{-1}. The results of this evaluation are given in table 4.

Table 4 - Evaluation of equation(2) expressed in units of 10^{-4} reciprocal deg.

Modulus	$\frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_V$	$\frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_P$	$-\frac{\beta K}{C}\left(\frac{\partial C}{\partial P}\right)_T$
C_{44}	-0.9	-5.02	+4.1
C'	+6.2	-5.64	+11.8
K^{-1}	-1.0	-2.34	+1.4

This table shows that the change in the elastic constants with temperature cannot be accounted for simply in terms of the change in volume brought about through thermal expansion. Lazarus[10] has previously pointed this out for K^{-1} of Aluminum and for this and other constants of other materials. For any metal, the elastic constants are considered as having contributions from three sources: The Fermi energy, the electrostatic energy, and the ion core interaction energy. Leigh[8] has pointed out that the lattice parameter of aluminum is such that the ion cores are too far apart for there to be an appreciable ion core interaction energy, and thus it appears that there is an explicit dependence on temperature involved in the Fermi and/or electrostatic energy. It is noted that this explicit dependence is different in both magnitude and

sign for the two shears corresponding to C_{44} and C'. There is no reason for the electrostatic energy to have an appreciable dependence on temperature so the contribution is probably from the Fermi term. Aluminum has three valency electrons per atom and the first Brillouin zone contains sufficient states for two of these provided each state contains two electrons. The excess electrons will occupy states in the second zone. As the temperature is increased, more excited electrons will spill over into the second zone and this would presumably change the Fermi energy contribution to the elastic constants.